Surfactant Enhanced Remediation (SER) of Contaminated Solid-liquid Drilling Wastes, Industrial Waste Water, and Groundwater (In-situ and Ex-situ Case Studies)



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FACT

90 to 95 % of All Contaminants Are Absorbed To Particles In Soil, Bed Rock and Groundwater Aquifers

Contaminant Absorption
Limits Availability of Contaminants For
All Forms of Remediation!

Sorption is the #1 Reason Why Many In-situ and Ex-situ Remediation Project are Slow, Costly or Fail.

!!!FACT!!!

Greater than 90% of all pump and treatment groundwater sites started in North America
10 years ago are still in operation today!

Ref: Bruce Tunnycliff, Vertex

!!!FACT!!!

F3 ands F4 Bioremediation is possible!

BUT - the sorption of these mid to heavy-end compounds onto the soil, drilling mud, bedrock, etc. make them less 'Bio-Available' for Bioremediation.

If you overcome Sorption F3 and F4 hydrocarbons are very biodegradable in soil and water!

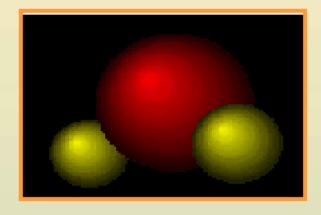
To better understand water treatment and or soil, solid waste, and drilling waste treatment, one needs to revisit their understanding of water...

This may hold to key to their successful clean-up...

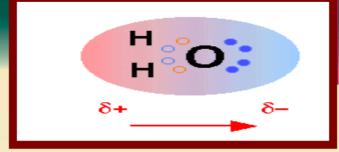
WATER H₂O Properties & Characteristic



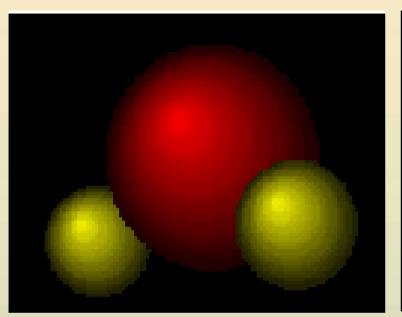
Introduction to Water Properties and Structure

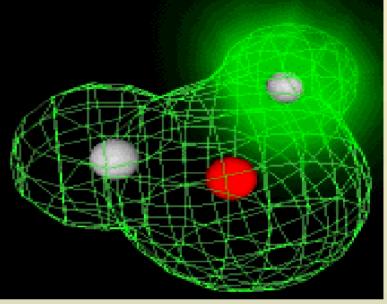


- ► Water has long been known to exhibit many *physical properties* that distinguish it from other small molecules of comparable mass.
- Chemists refer to these as the "anomalous" properties of water, but they are by no means mysterious
- All are entirely *predictable* consequences of the way the size and nuclear charge of the *oxygen* atom conspire to *distort the electronic charge clouds of the atoms of other elements* when these are chemically bonded to the oxygen.



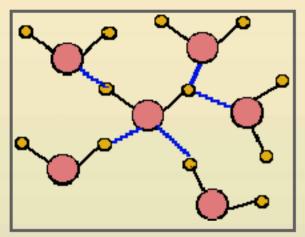
- A covalent chemical bond consists of two atoms that *share a pair of electrons* between them.
- ▶ In the water molecule H₂O, the single electron of each H is shared with one of the six outer-shell electrons of the oxygen, leaving *four* electrons which are organized into two non-bonding pairs.
- ► Thus the oxygen atom is surrounded by four electron pairs that would ordinarily tend to arrange themselves as far from each other as possible in order to minimize repulsions between these clouds of negative charge.
- ► This would ordinarily result in a tetrahedral geometry in which the angle between electron pairs (and therefore the H-O-H bond angle) is 109°.
- ► However, because the *two non-bonding pairs remain closer to the oxygen* atom, these exert a stronger repulsion against the two covalent bonding pairs, effectively *pushing the two hydrogen atoms closer together*. The result is a distorted tetrahedral arrangement in which the H—O—H angle is 104.5°.

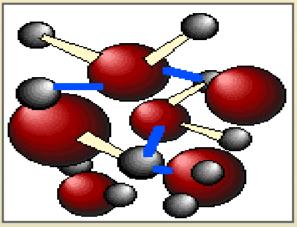


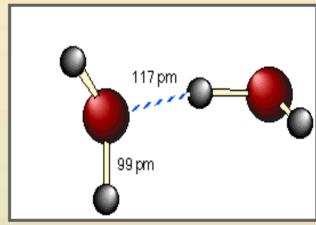


Water H₂O Molecule Representations Covalent Bond Between Oxygen and Hydrogens

These two computer-generated images of the H_2O molecule come from calculations that model the electron density distribution in molecules. The outer envelopes show the effective "surface" of the molecule.



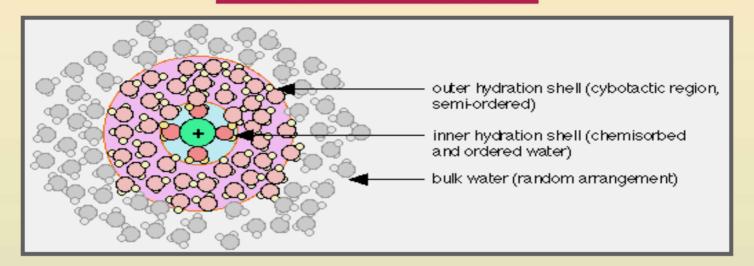




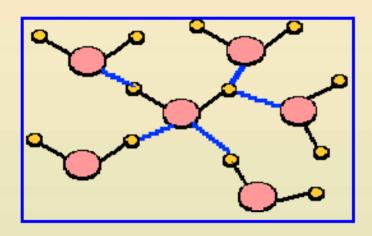
- ► <u>Hydrogen Bonding</u> (*in-blue*) Exists Between Neighbouring Polar Water Molecules. The Bonding Exists Between The Oxygen & Hydrogen Atoms *Pulling* H_2O *Molecules Together*.
- ► They Forming And Break Rapidly (nano-seconds). Hydrogen Bonding Giving Rise To Waters Surface Tension, Its Physical Properties, And The Insolubility Of Non-Polar NAPL Compounds.
- ► This Property Supports The Hydrophilic (*Water Liking*) Portion Of The Surfactant Molecules that renders NAPL Compounds Miscible In Water.

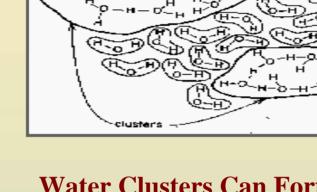
Water = Hydrogen Bonding!

- ▶ When thinking about water and its chemical and physical characteristics, one must understand they are directly the result of Hydrogen Bonding!
- ► Hydrogen Bonding dictates water's behavior and how it interacts with other substances including organic chemical contaminants
- ► If the NAPL will or will not dissolve, and/or migrate within soil and/or groundwater plume, and their rate of transport._



- ► Water molecules interact strongly with non-hydrogen bonding species as well. A particularly strong interaction occurs when an ionic substance such as sodium chloride (NaCl, ordinary salt) dissolves in water.
- ightharpoonup Owing to its *high polarity*, *the H_2O* molecules closest to the dissolved ion are strongly attached to it, forming what is known as the *primary hydration shell*.
- ▶ Positively-charged ions such as Na+ attract the negative (oxygen) ends of the H_2O molecules, as shown in the diagram below.
- ► The ordered structure within the *primary shell creates*, *through hydrogen-bonding*, *a region in which the surrounding waters are also somewhat ordered*; this is the outer hydration shell, or cybotactic region.
- ► Water H₂O Molecule Representations Covalent Bond Between Oxygen and Hydrogen's.





Hydrogen Bonding Between
Polar Water Molecules (*in-blue*)
Pulling Water Together
Between Neighbouring H₂O.

Water Clusters Can Form Form As A Result That Range In Size & Complexity

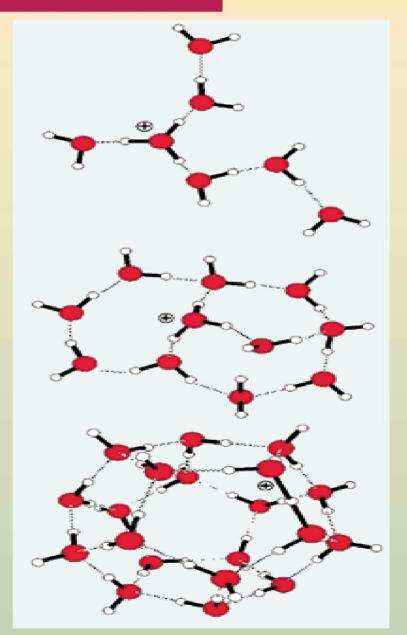
- ► <u>Hydrogen Bonding</u> Is What Gives Rise To The Insolubility Of Non-Polar NAPL Compounds, And Why the Hydrophilic (*Water Liking*) End Of Surfactant Molecules Are So Effective In Rendering The NAPL Compounds Miscible In Water.
- ► <u>Clustering</u> of water molecules affects the K (Conductivity) of water in various soil types!

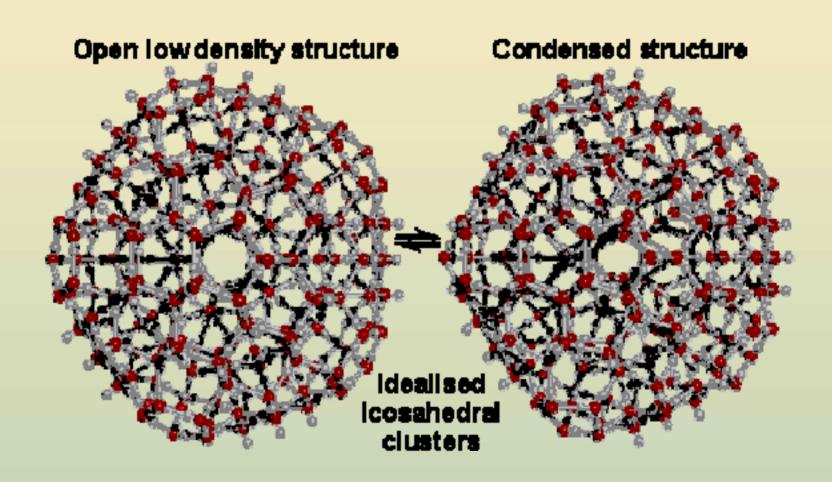
Formation of hydrogen bonds between like water molecules...

This results in the formation of Water Clusters which can get large in size...

So water is not just H₂O...

So we have to change the way we think of water form a practical stand point.





This affects many of the chemical and physical properties of water!

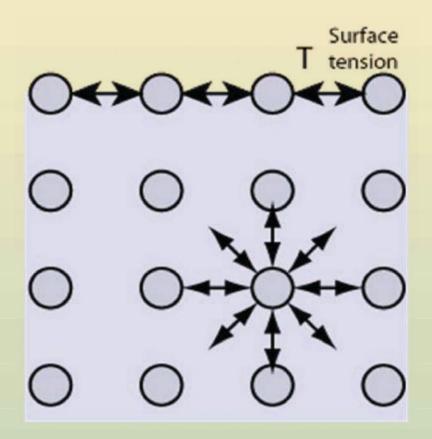
- Boiling Point
- Freezing Pint
- What will or will not dissolve in water
- Viscosity
- K (Conductivity) in soils
- Surface tension
- Density (Density of Fresh < Salt Water)</p>
- Why some water and soil treatments do not work...

Surface Tension

- ► The <u>cohesive</u> forces between liquid molecules are responsible for the phenomenon known as surface tension.
- The <u>molecules at the surface</u> do not have other like molecules on all sides of them and consequently they cohere more strongly to those directly associated with them on the surface. This forms a surface "film" which makes it more difficult to move an object through the surface than to move it when it is completely submersed.
- Surface tension is typically measured in <u>dynes/cm</u>, the force in dynes required to break a film of length 1 cm. Equivalently, it can be stated as surface energy in ergs per square centimeter.
- ► Water at 20°C has a surface tension of 72.8 dynes/cm compared to 22.3 for ethyl alcohol, and 465 for mercury.

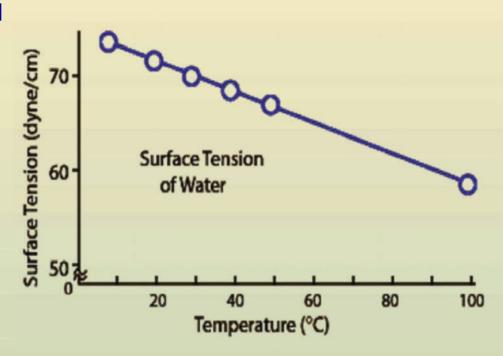
Cohesion and Surface Tension

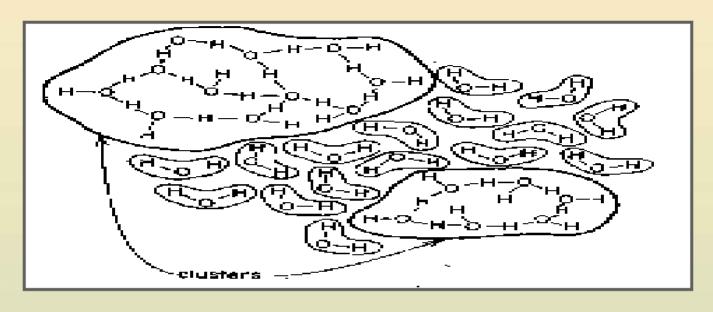
- ► The <u>cohesive</u> forces between Molecules down into a liquid are shared with all neighboring atoms.
- ► Those on the surface have no neighboring atoms above, and exhibit stronger attractive forces upon their nearest neighbors on the surface.
- ► This enhancement of the intermolecular attractive forces at the surface is called *surface tension*



Surface Tension of Water

- ► The <u>surface tension</u> of water is 72 dynes/cm at 25°C. It would take a force of 72 dynes to break a surface film of water 1 cm long.
- ► The surface tension of water decreases significantly with temperature as shown in the graph. The surface tension
- Arises from the <u>polar nature</u> of the <u>water molecule</u>. Hot water is a better cleaning agent because the lower surface tension makes it a better "wetting agent" to get into pores and fissures rather than bridging them with surface tension.
- Soaps and detergents further lower the surface tension.





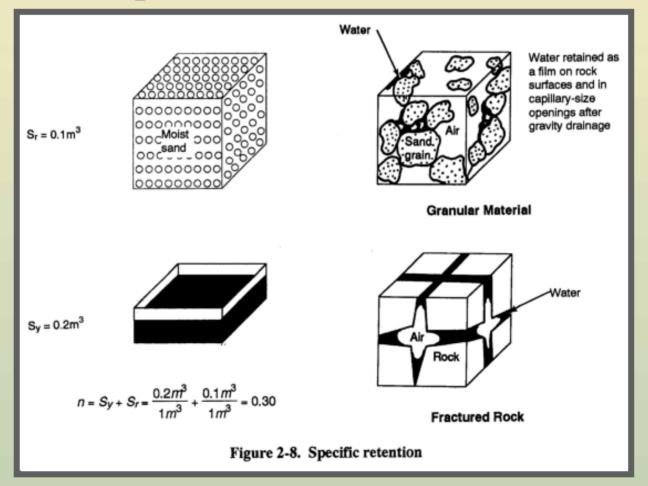
- The lower the temperature of water, the higher the surface tension (See Graph);
- ► The higher the surface tension the greater the formation & size of water clusters (Groundwater is usually between 6-10 °C); and
- ► The larger the water clusters, the lower the associated K value in all soil types (Sand 1x10⁻³ cm/sec, Silty-sand 1x10⁻⁴ cm/sec, Silt 1x10⁻⁵ cm/sec, Silty Clay 1x10⁻⁶ cm/sec Clay 1x10⁻⁷ cm/sec).

WATER CLUSTERS

- ► Theoretical models suggest that the average cluster may encompass as many as 90 H₂O molecules at 0°C, so that very cold water can be thought of as a collection of ever-changing ice-like structures.
- ► At 70° C, the average cluster size is probably no greater than about 25.
- ► Groundwater is between 6 to 10°C, so moderate to large clusters. Macro-clusters also form!
- ➤ So water clusters are a reality in soil and ground water remediation, and have a direct affect on K

SORPTION

Adsorption and Absorption Properties and Characteristics



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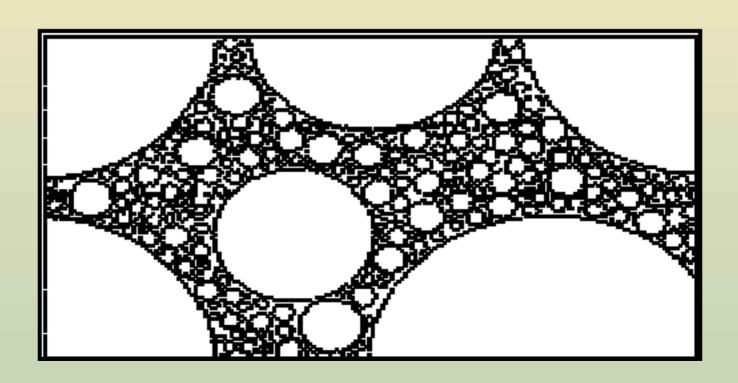
Sorption and Partitioning (Kd):

- **Sorption** refers to the property of a solute to either *attach* to the *surface* of a solid (**adsorption**) and/or then *penetrate* the solid (**absorbtion**).
- Sorption results in a reaction between the concentration of solute in the aqueous phase, and the concentration on or in the solid. At equilibruim, the partitioning of solutes between liquid and solid phases in the porous medium can be described by an equilibrium constant, **Kd**
- partitioning causes a *retardation* in the contaminant front. Because solutes are almost always slower than the groundwater, they are said to be *retarded*. Exceptions: halogens chloride, iodide, fluoride

- The <u>sorption of a contaminant</u> is one of the significant processes that <u>can hinder the remediation of a soil and ground water</u> aquifer system.
- Sorption is defined as being the *attraction of an aqueous species to the surface of a solid*.(Alley, 1993).
- In ground water the sorbing species, usually an *organic compound*, is called the *sorbate*, and the solid media, usually *soil*, to which the sorbate is attracted is known as the *sorbent*.
- The <u>amount of sorption</u> that occurs <u>in soil and or groundwater</u> is <u>dependent on particular characteristics of the sorbate and sorbent</u>. The amount of sorption that takes place on organic matter also follows various isotherms or kinetic rates.
- Sorption tends to cause contaminants to move more slowly than the groundwater, therefore the effects must be taken into consideration when calculating how far the contaminant has traveled in a given time period.

Sorption (Absorption and Adsorption) of Contamination in Soil Matrix

Soil & Water Remediation Must Address This To Be Successful.

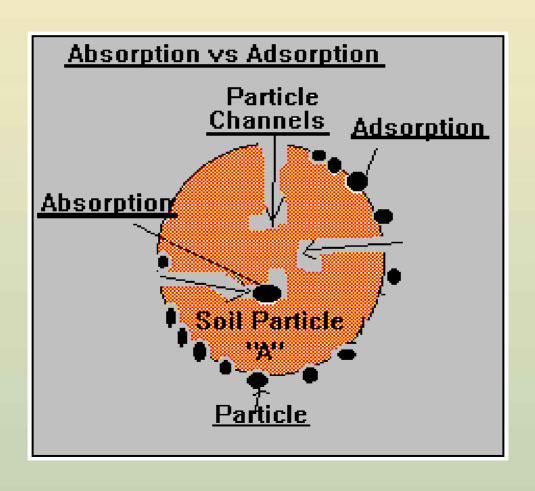




Adsorption vs. Absorption

- Sorption reactions generally occur over a short period of time, however if the adsorbed contaminant begins to be incorporated into the structure of the sorbent, a slow occurring reaction, known as absorption, begins to take place.
- ▶ To be more precise, the difference between adsorption and absorption is that adsorption is the attraction between the outer surface of a solid particle and a contaminant, whereas absorption is the uptake of the contaminant into the physical structure of the solid.
- This figure shows the primary differences between intra-particle absorption versus surface adsorption.
- The main difference being that some contaminant particles are attracted to the outer surface of the soil particle, while another has been actually incorporated into the particle's structure.

Adsorption vs. Absorption



Class Exercise IV Sorption Demonstration

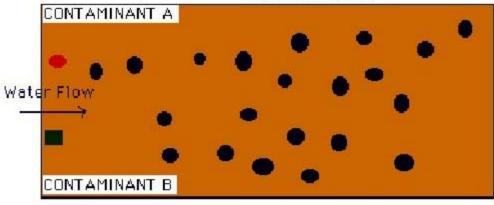
(Animation)

The following animation sequence displays how sorption can affect two separate particles' velocity.

Basically, the animation shows a vertical cut from a soil column, interspersed particles of organic matter, and two contaminants that are moving through the soil.

THE VELOCITIES OF TWO CONTAMINANTS
ONE IS SORBING---ONE IS NOT

SOIL PARTICLES



FACT

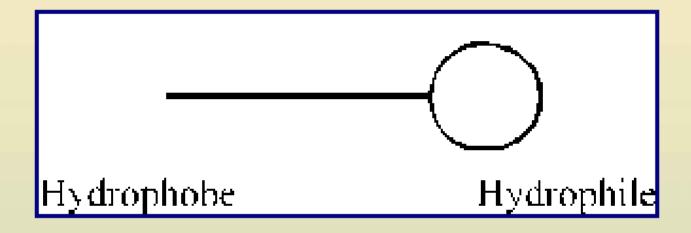
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Sorption Limits 'Availability' of Contamination For

- Removal by <u>Pump and Treatment</u>;
- Availability for <u>Bioremediation</u>;
- Availability for <u>Oxidation and Reduction</u>

Ivey-sol Desorbs Contamination Improving Insitu and Ex-situ Remediation Methods

Now To Understand
How Surfactants
Can Aid The Treatment of
Water, Soils, Solid Wastes and
Drilling Wastes...



Surfactant Chemical Structure

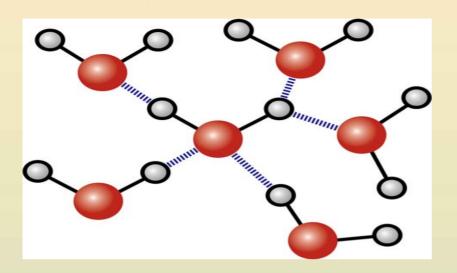
Hydrophilic (water loving) and Hydrophobic (water hating oil-liking) Groupings Allow For Surface Interaction
With Many Contaminants

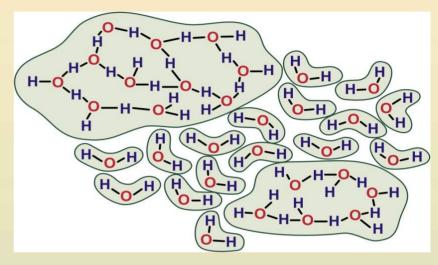
Classes Of Surfactants

- Anionic: They have one or more negatively (-) charged groupings. They have very good detergent ability and are commonly used as laundry detergent.
- <u>Cationic</u>: They have one or more positively (+) charged groupings. They typically have poor detergency, but are well suited for use as germicides, fabric softeners, and emulsifiers.
- Amphoteric: They contain both anionic and cationic groupings and have the characteristics of both anionic and cationic SAA. They work well at neutral pH and are found in products such as hair shampoo, skin cleaners, and carpet shampoo.
- Non-ionic: As their name implies, they have no ionic constituents or groupings. They are the largest single group of SAA and have a correspondingly wide range of chemical characteristics and application. Ivey-sol surfactant mixtures, are non-ionic and have the unique ability to selectively desorb contamination (LNAPL, DNAPL's, PAH, PCB, DCE, TCE, PCE), etc.

Ionic Surfactants make up >99% of the surfactant used around the world.

In this regard Ivey-sol is very unique.





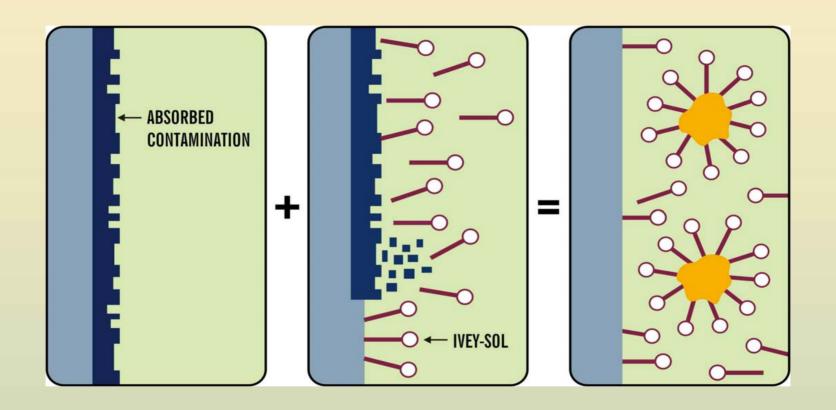
Hydrogen Bonding Between
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Water Clusters Can Form Form As A Result That Range In Size & Complexity

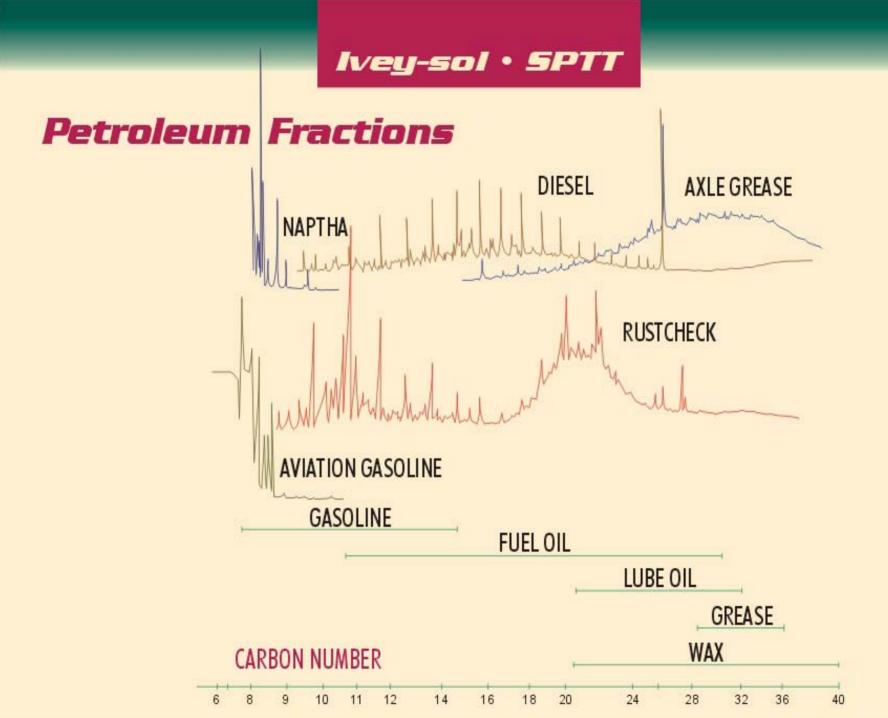
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Ivey-sol Lowers The Surface Tension of Water From 72 Dynes to <30 dynes

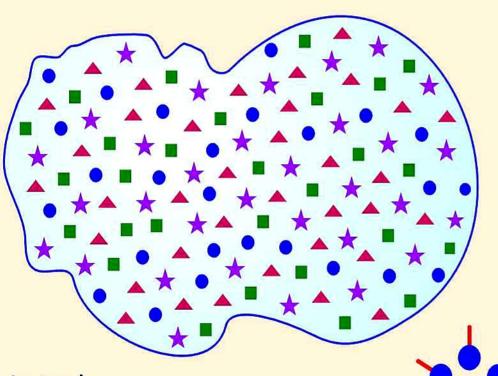
This increases the wetting ability of the water when present, making Ivey-sol® application possible in fine grain soils improving Water Permeability (K).



Ivey-sol Interaction With Oil On A Surface With Partial Micelle Encapsulated of Oil Droplet (Ivey-sol is Effective Below The CMC)



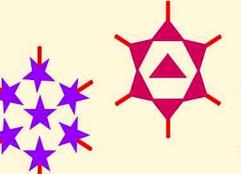
Selective Micelle Encapsulation of Contamination

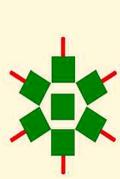


- Selective Micelle Formation
- Encapsulation and increased solubility
- Applicable for full LNAPL and PAH range
- Ivey-sol mixture is taylored to type/range of contamination being treated

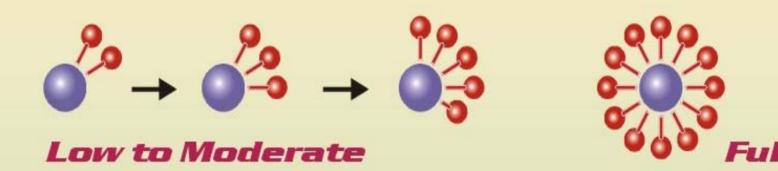
Legend:

- Aromatics
- Cyclic Alkanes
- **Alkanes**
- PAHs

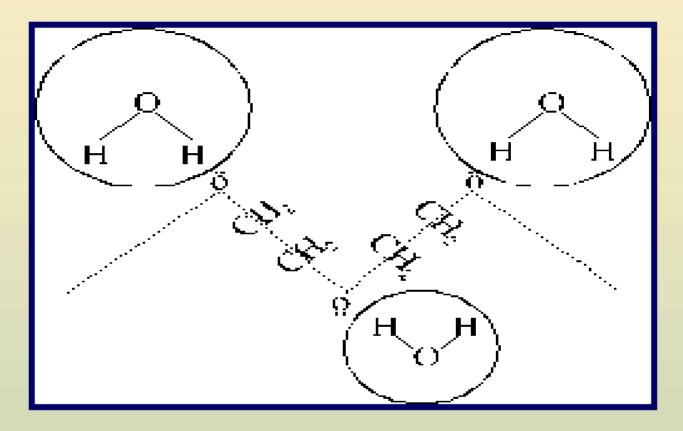




Encapsulation Effects



- Liberation of contamination can be effected with low to moderate encapsulation. Hence, low SPTT concentrations are effective.
- As partial encapsulation is predominant due to injection concentrations, no negative effects are realized at the treatment system (e.g., GAC, Air Stripping, Bio-Reactors, Membrane Separation, etc.)



Ivey-sol's Hydrophilic Interaction With Water (H_2O) Utilizing Hydrogen Bonding Effects To Aid Dissolving Contaminants in Water

Remediation By-Products

- **USEPA & Environment Canada Are Concerned About By-Products**By-Products Produced During Chemical & Biological Remediation.
- Chemical Reactions Are Not 100%! Hence They Giving Rise To The Formation of By-Products During Remediation.
- Chemical Oxidation and Reduction of Organic Contaminants

 Will Produce By-Products. (Often Unknown and/or Missed During Laboratory

 Analysis. The Old "Out of sight out of mind" Philosophy!)
- RISKS: Remediation By-Products Can Be More Toxic Than The Target Contamination. Example: The well published Biodegradation of TCE forming Vinyl Chloride, that was 15+ times more toxic than the original TCE contamination.

Ivey-sol does not alter the chemical structure of contaminants. Hence, no by-products formed averting by-product risks.

APPLICATION RANGE

LNAPL

Full LNAPL (F1,F2, F3, and F4) Range Including: BTEX, Gasoline, Diesel, Motor-Oil, Bunker-C, MTBE, PAH's, etc.

DNAPL

25 Fold (+) Increase In Solubility & Recovery Rate. This includes Compounds Like: PCE, PCB, TCE, TCA, CTC, TCM, PCP, & Various other Cl / Br Solvents

Heavy Metals

Transition metals, including organo-metalic complexes, and radio-active metals associated with NORMS.



Fuel-oil - Bunker-C - Gasoline Dissolved In Water With Ivey-sol

PAH Soil Remediation

Parameters	Baseline	Ivey-sol 106	% Reduction
PAH'S	ppm	ppm	ppm
1-Methylnaphthalene	130	5	96.1%
2-Methylnaphthalene	220	6	97.3%
Acenaphthene	46	6.1	86.7%
Acenaphthylene	140	6.4	95.4%
Anthracene	190	19	90.0%
Benzo(a)anthracene	100	14	86.0%
Benzo(a)pyrene	74	9	87.8%
Benzo(b)fluoranthene	54	6.3	88.3%
Benzo(ghi)perylene	21	3.3	84.3%
Benzo(k)fluoranthene	54	6.3	88.3%
Chrysene	100	13	87.0%
Dibenzo(a,h)anthracene	9.6	1.2	87.5%
Fluoranthene	230	26	88.7%
Fluorene	190	12	93.7%
Indeno(1,2,3-cd)pyrene	35	4.5	87.1%
Naphthalene	560	9.7	98.3%
Perylene	20	1.6	92.0%
Phenanthrene	420	37	91.2%
Pyrene	170	19	88.8%

Treatment of Chlorinated Contaminated Fine Grain Soil

Chlorinated Compounds	Baseline Mg/kg	Treatment No. 1	Reduction (%)	Treatment No. 2	Reduction (%)	Total Reduction				
1,2-Dichlorobenzene	8,300,000	490,000	94%	56000	89%	99.33%				
1,3-Dichlorobenzene	1,100,000	45,000	96%	8100	82%	99.26%				
1,4-Dichlorobenzene	2,900,000	110,000	96%	14000	87%	99.52%				
Chlorobenzene	170,000	12,000	93%	150	98.80%	99.91%				
Styrene	1200	74	94%	ND	>99.99%	>99.99%				
TCE	590	41	93%	ND	>99.99%	>99.99%				

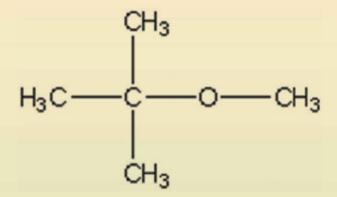


Common name: Methyl Tertiary Butyl Ether

Molecular Formula: C₅H₁₂O

Chemical name: 2-Methoxy-2-methyl-propane

Solubility: In water, 51.26 g/L @ 25°C



Usage: Introduced as an octane replacement for tetraethyl lead in the 1970s, used as an oxygenating agent added to ~30% of U.S. gasoline supply to reduce carbon monoxide emissions of automobiles and meet air quality standards. Almost the entire production of MTBE (9.1 billion pounds in 1992 by 27 companies in the United States) is used as a gasoline additive.

In 1999, it was estimated that between 5 and 10% of community drinking water supplies in high MTBE use areas had detectable MTBE levels; as many as 9000 community water supply wells in 31 states many be affected.

MTBE is considered a potential human carcinogen.

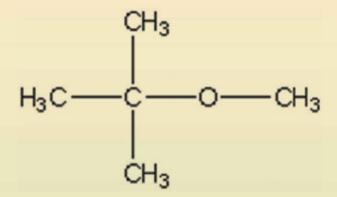
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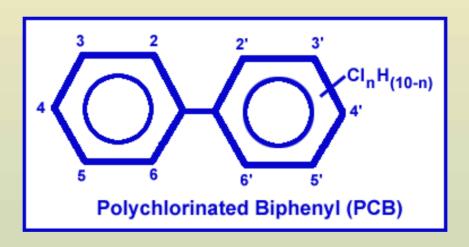
Recent Research Has Confirmed *Ivey-sol* Increases The Controlled Solubility and Rate of *MTBE* Recovery From Soils, Bed Rock, and Groundwater

By > 740%

Reference: Dr. Davis Craft, University of Alberta (2004)

PCB's

Ivey-sol Increases The Solubility of PCB's by > 900%



Based on Research and Development Work Completed in 2005 by Dr. David Craft (NRC) & Ivey International

FACT

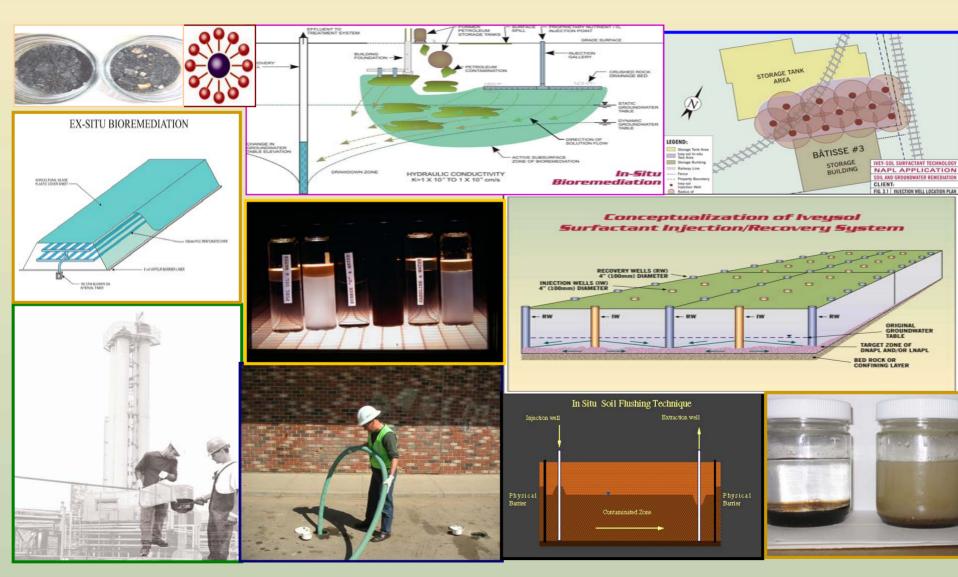
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Surfactant Remediation SER SEB SEO



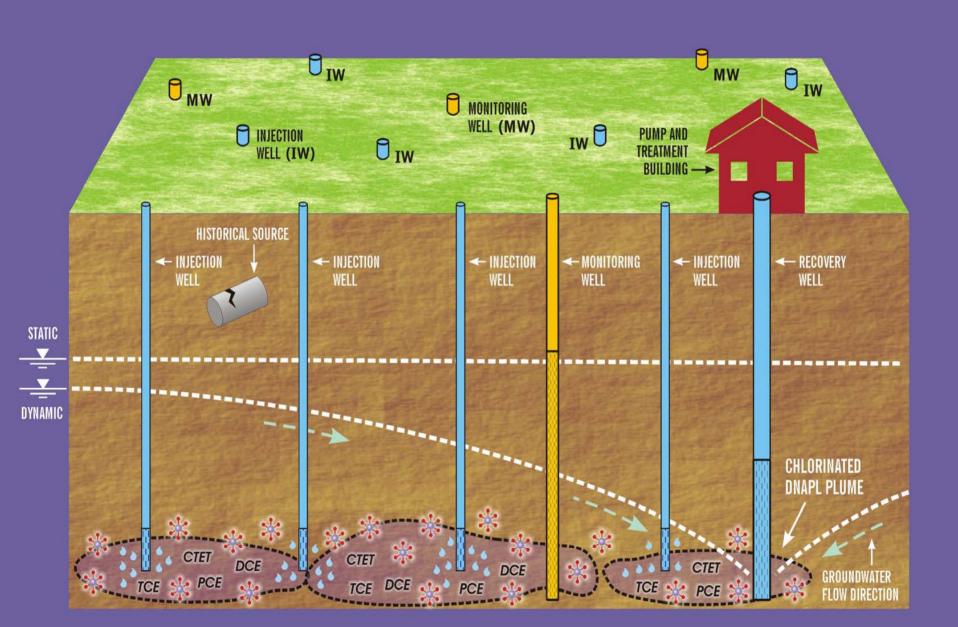
SER®

The application and use of Surfactants for soil and groundwater remediation is known as

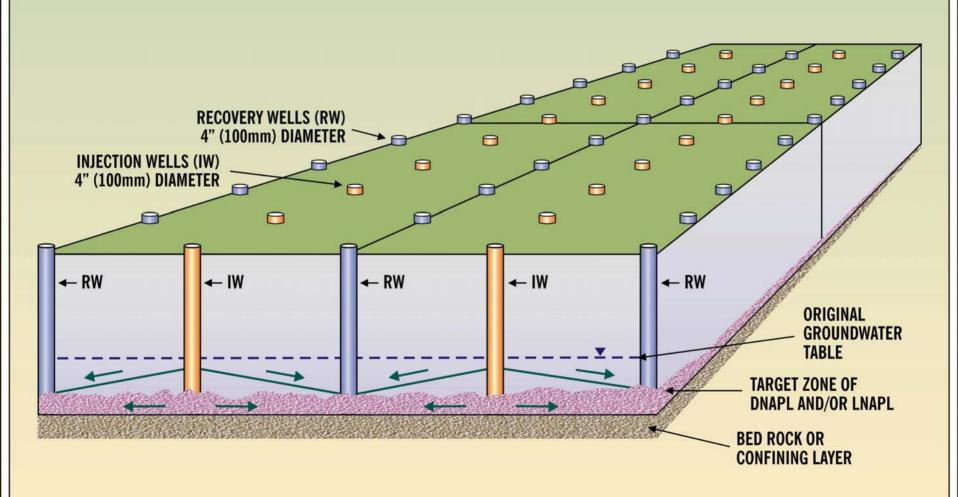
SER - Surfactant Enhanced Remediation

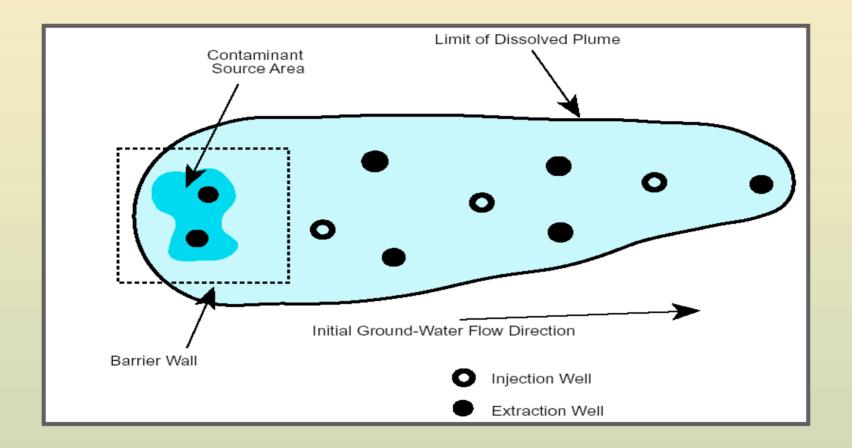
IN-SITU REMEDIATION

To design a good 'Remediation Action Plan' you need a good quality Phase II Site Investigation.

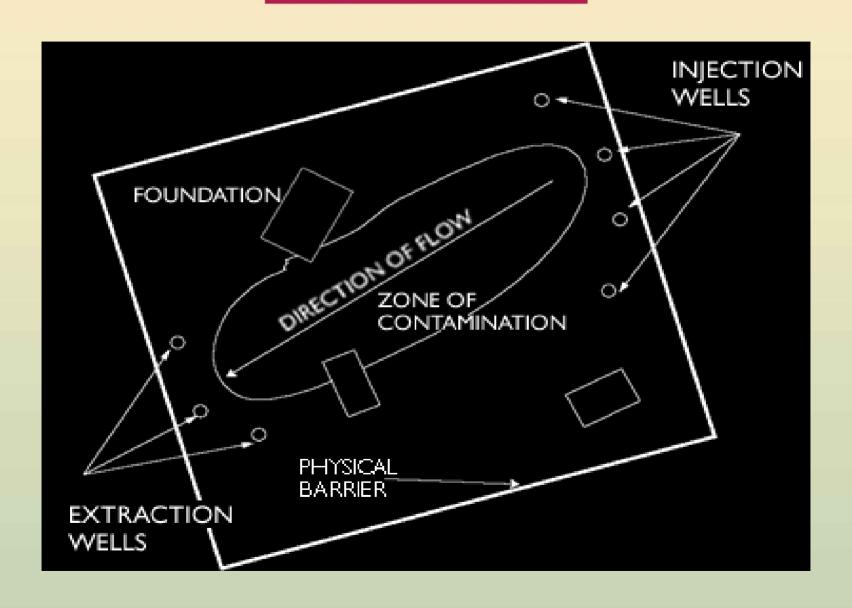


Conceptualization of Iveysol Surfactant Injection/Recovery System

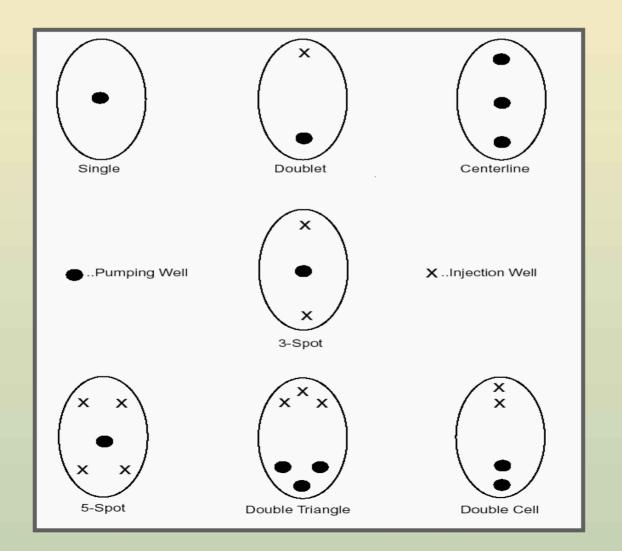




Plan view of a mixed containment-restoration strategy. A pump-and-treat system is used with barrier walls to contain the ground-water contamination source areas (e.g., where NAPL or waste may be present) and then collect and treat the dissolved contaminant plume (Cohen et al., 1994).

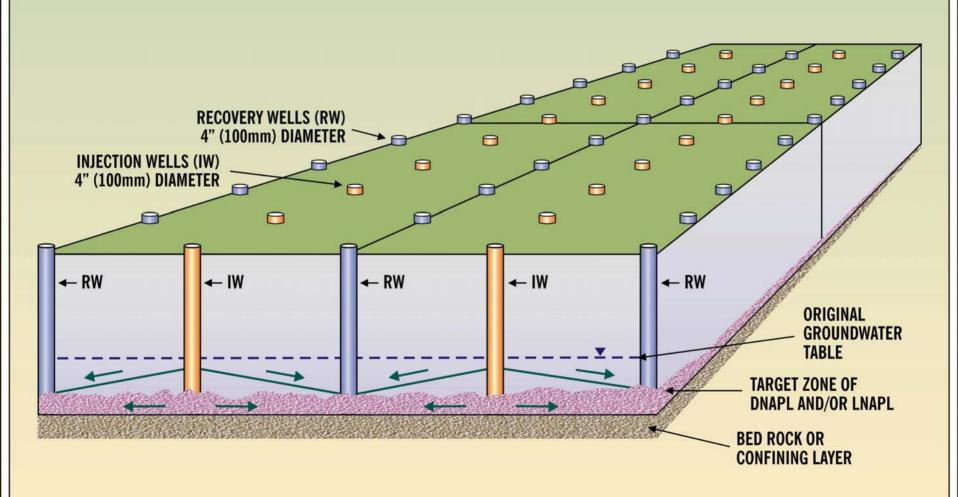


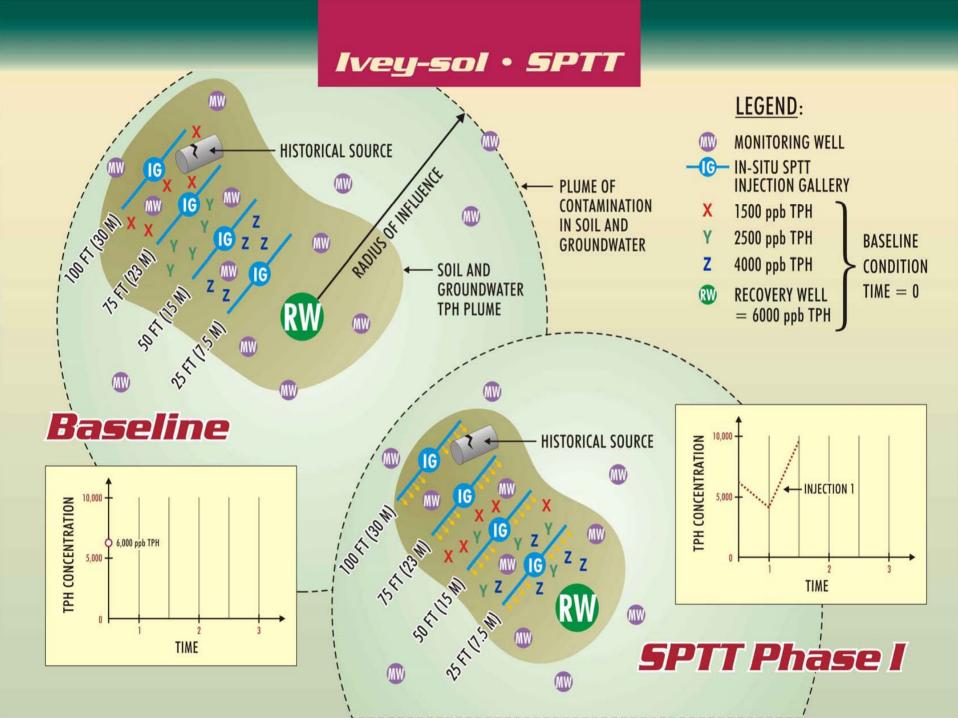
Pumping Injection Well Patterns

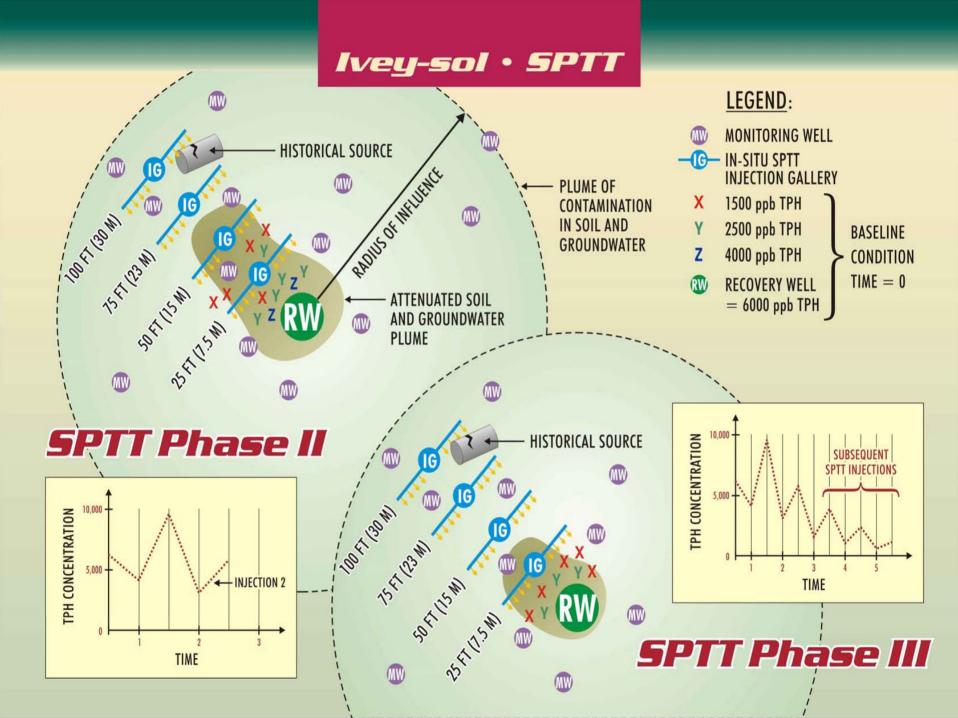


Major types of pumping/injection well patterns (Satkin and Bedient, 1988).

Conceptualization of Iveysol Surfactant Injection/Recovery System





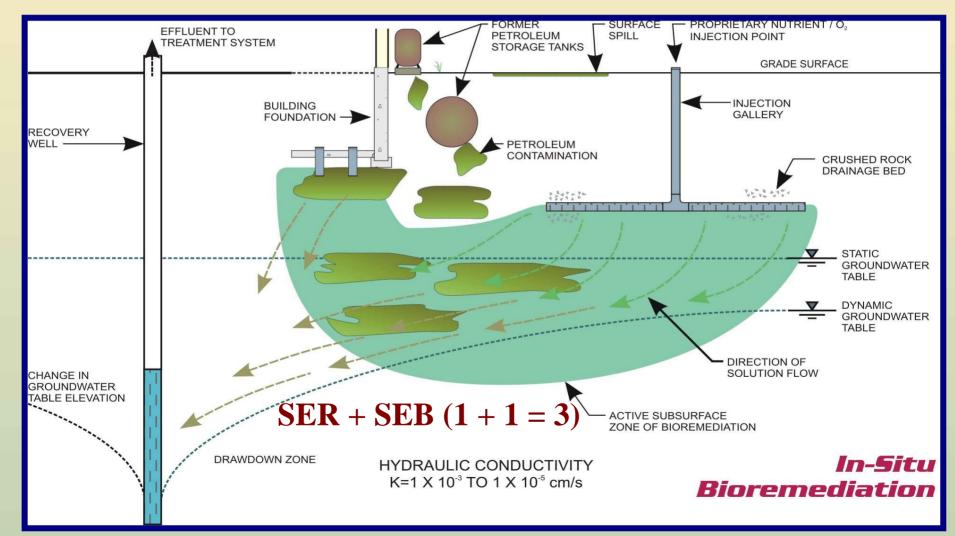


Surfactant Enhanced Oxidation (SEO)

- Ivey-sol Surfactants are applied to PCB contaminated soils to desorb PCBs
- Following de-sorption of PCB's a water soluble oxidizing chemical (Agent) is applied.
- PCB levels reduced to clean-up standards with some samples coming back Non-Detectable.
- When oxidizers are used alone, efficiency was < 35%.

Reference: 2005 Project Collaboration
Ivey International & National Environmental Contractor

In-Situ SEB Surfactant Enhanced Bioremediation



EX-SITU REMEDIATION



Ex-Situ Soil Treatment Unit
Small To Large Scale LNAPL & DNAPL

Soil Remediation

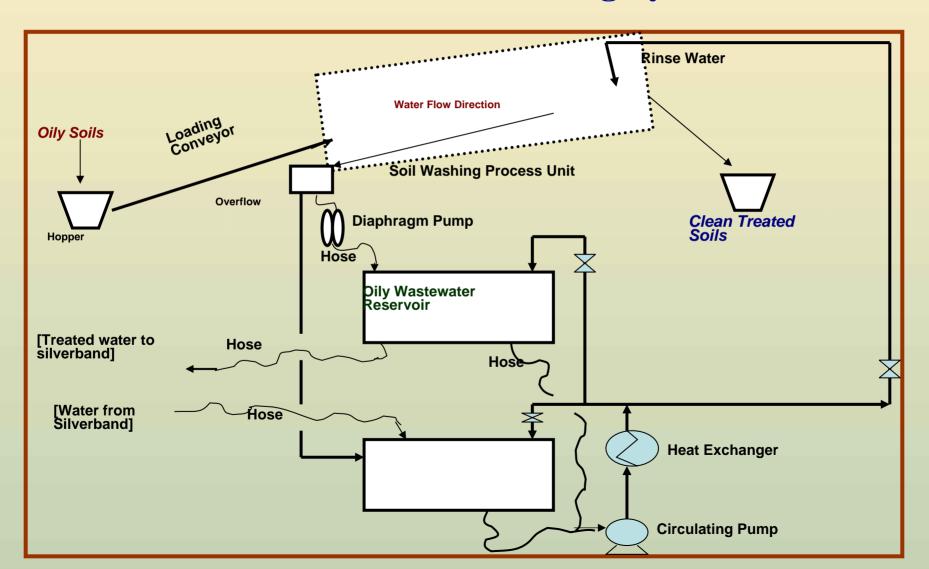
(Mobile 3 to 35 cubic yards units)





Refinery Site - Soil Contamination
Clean-up Objective: < 3% Mineral Oil & Grease

SER Ex-situ Soil Washing System



Alberta Canada Oil Refinery Site (>5000 Tons)

Contaminated soil with a baseline concentration of 40,000 ppm (4%). Ex-situ Ivey-sol Soil Washing SER Process achieved applicable soil remediation site objectives. Project data set provided below showing pre and post soil washing remediation results with time based sample analysis.

Soil Parameter	Base Line	5 Minutes	7 minutes	Reductions
CCME F1 C6-10	72 ppm	< 1 ppm	< 1ppm	100%
CCME F1 BTEX	71 ppm	< 1 ppm	< 1ppm	100%
CCME F2 C10-16	417 ppm	35 ppm	21 ppm	95%
CCME F3 C16-34	13, 600 ppm	1,600 ppm	826 ppm	94%
CCME F4 C34-50	5,060 ppm	512 ppm	259 ppm	95%
CCME F4 C34-50+	13,000 ppm	571 ppm	290 ppm	98%

Note: CCME = Canadian Council of Ministers for the Environment. From CCME Soil and Water Clean-up Guideline Parameters.



Pre and Post Ivey-sol Treatment

Effective Removal of Heavy-end Hydrocarbons.

Ex-Situ Soil Treatment Sydney Australia



Ex-situ Soil Treatment SEO & SEB

















Tank Cleaning Applications
Before & After Ivey-sol® Cleaning



Oil Recovery Potential

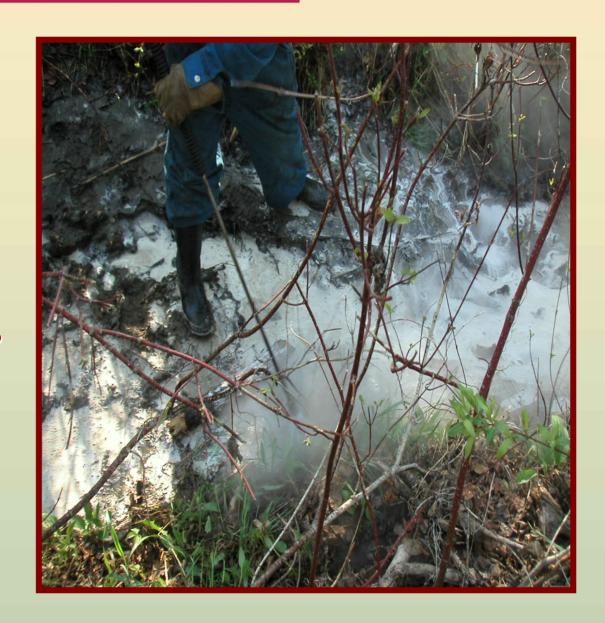
- Coagulants & Flocculants were used to precipitate the petroleum from the post treated water
- Upper water layer is clarified and available for re-use.
- Hence water use is less a limiting an issue as a result.
- Passing the precipitate through a Filter-press would allow for the recovery of the target hydrocarbons. These may be of economic value.



Stream and Shoreline Spill Clean-up With (Ivey-sol ®).

Application via highpressure spray to liberate hydrocarbons from stream-bed sand, rock and vegetation.

Removal of dissolved wastes from localized area via Vacuum suction hose.

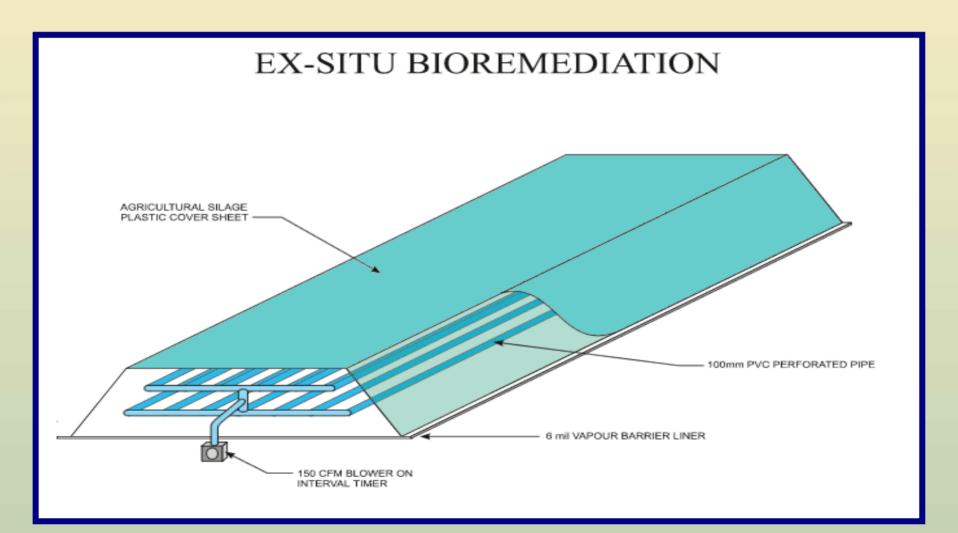


Oil & Gas Well Frac-Sand Waste Treatment (Ivey-sol®)

Sample From Alberta, Western Canada



Ex-Situ SEB Surfactant Enhanced Bioremediation (F3 &F4)





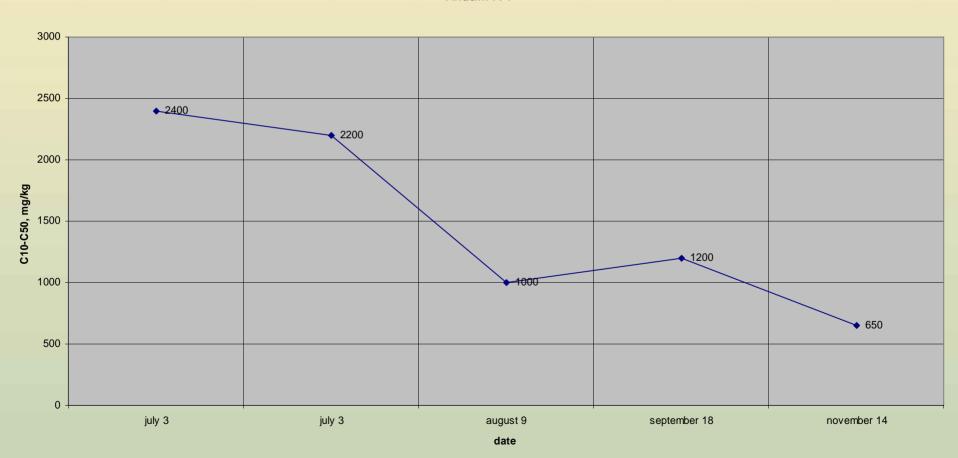




SEB Ex-situ Soil Remediation Project

Quebec, Canada

Andain A-1



SEB Fine Grain F3 & F4 Remediation

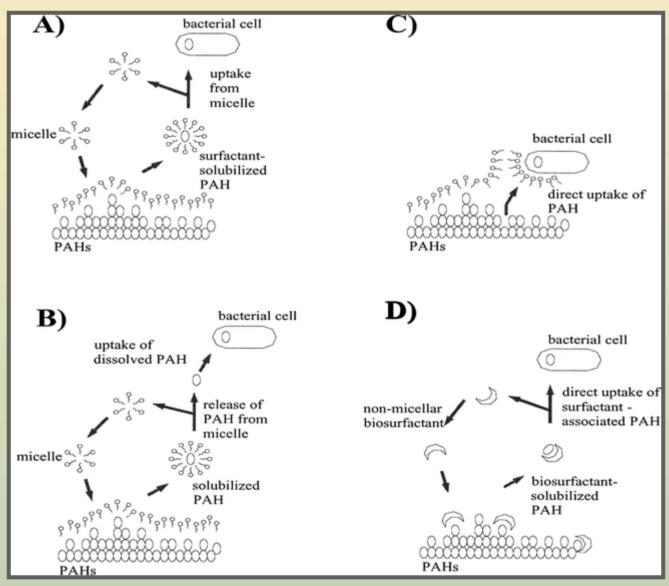


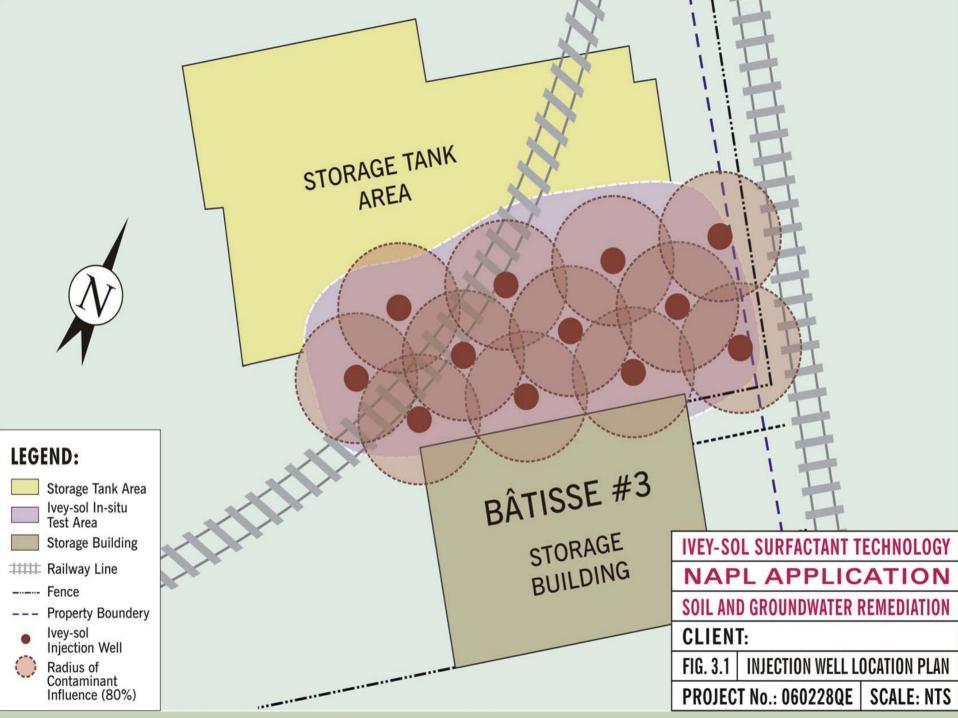






SEB Mechanism For PAH's



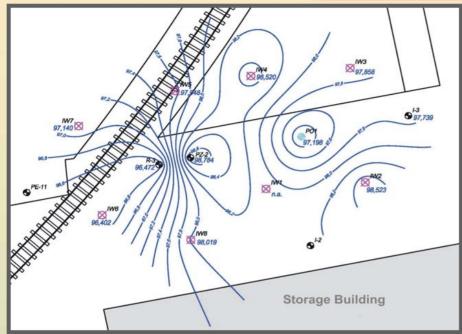






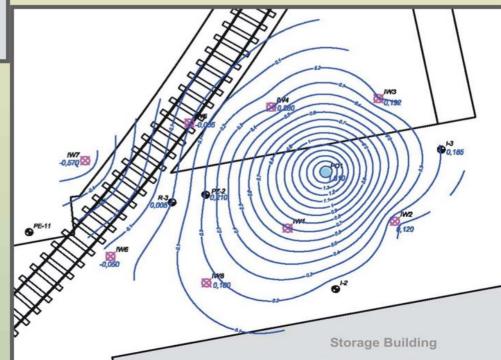






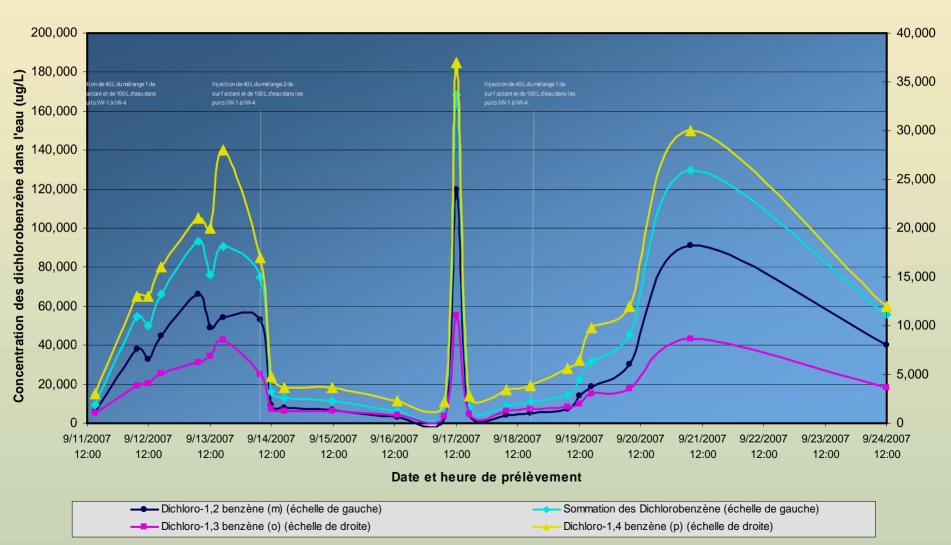
Pre-Injection Hydraulic Containmnet Conditions Static Ground Water Gradient

Pre-Injection Hydraulic Conditions
Post Vacuum Extraction System
Hydraulic Stabilization





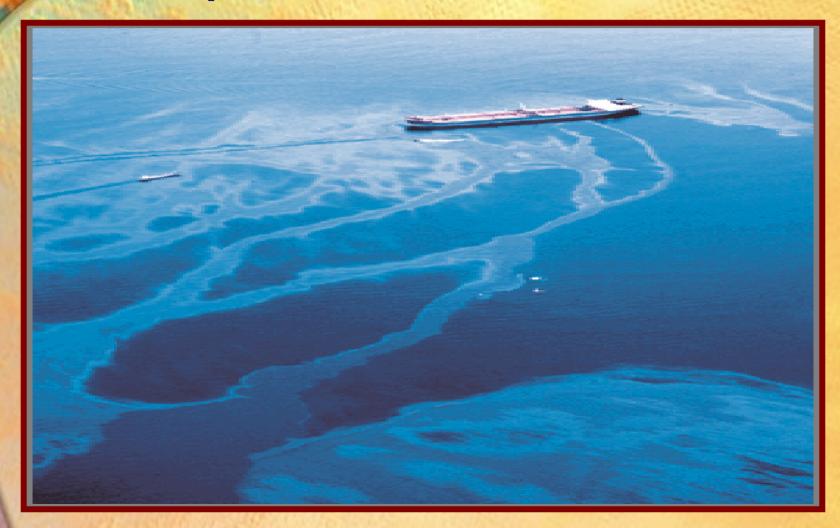
Variation de la concentration des dichlorobenzènes en fonction du temps au puits PO-1



Pilot Scale Project Test Results

- ► The In-situ Ivey-sol Surfactant Application Significantly increased the rate of DCB recovery;
- Increased DNAPL (DCB = Dichlorobenzene) recovery by 800-1200%;
- Recovered kg(s) of DCB over a three (3) injection pilot Scale Application in one-week;
- Client was pleased as all three previous remediation techniques applied failed at a significant cost to the client; and
- Client has awarded the environmental consultant the contract to proceed with full scale application.

Oil Spill As Viewed From The Air



Dispersant Applications

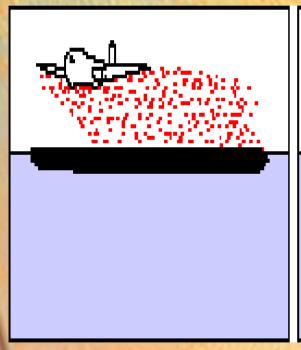


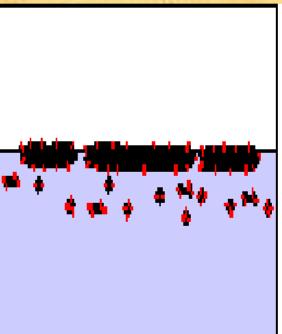


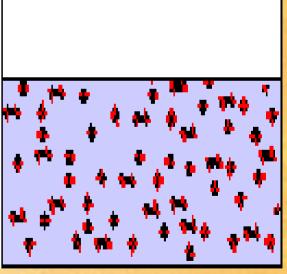




Mechanism Aerial Dispersion







Before and After Dispersant Shore Line Clean-up



1989 - Exxon Valdez 40,000 tons of oil spilled



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